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Determination of the Equilibrium Constant for the Acetaldehyde-Bisulfite Addition Compound

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DETERMINATION OF THE EQUILIBRIUM CONSTANT
FOR THE
ACETALDEHYDE-BISULFITE ADDITION COMPOUND

by

Mark B. Richard

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of the requirements for
Honors in the Department of Chemistry

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ABSTRACT

Richard, Mark B. Determination of the equilibrium constant for the acetaldehyde-bisulfite addition compound, March, 1985.

Synthesis of the addition compounds of formaldehyde, acetaldehyde, acetone, and propionaldehyde with sodium bisulfite was achieved using the method of Stewart and Donnally. Recognition of a water contamination led to a method for determining purity using the integrations from NMR spectroscopy. An equilibrium constant for the acetaldehyde-bisulfite addition compound was determined using the method of Dasgupta. A value of 6.3×10^{-5} was determined at a pH of 4.7. This value correlates well in magnitude when compared to the value of 1.56×10^{-5} for the formaldehyde-bisulfite addition compound at pH 5.0 determined by Dasgupta and also with Stewart and Donnally's value of 1.06×10^{-4} determined for the benzaldehyde-bisulfite addition compound at pH 4.77.

I would like to take this opportunity to thank Professor Hull for all the help he has given in making this project possible. His patience and knowledge have given me the chance to experience the failures and rewards of learning through independent research. My thanks is also extended to the Chemistry Department at Union College for all their help and understanding during my four years of undergraduate study.

Sincerely,

Mark B. Richard

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INTRODUCTION

Interest in the atmospheric sulfur cycle has grown recently. Evidence indicates that an increase in levels of atmospheric sulfur has increased rain acidity and has reduced the overall quality of the air(1,2,3). More specically, it is an interest in the oxidation of S(IV) to S(VI). In areas where high levels of S(VI) are to be found, namely the east coast of the United states and Canada and certain parts of Europe, the increased acidity of rain due to this oxidation process has increased the acidity of many body's of water in these areas and has resulted in harmful effects to these ecosystems. The hope for a better understanding of this problem has directed a considerable amount of research into this area.

It is now known that there exist both direct and indirect sources of sulfur dioxide to the atmosphere(1). A considerable number of biogenic processes are known to emit sulfur into the atmosphere in such forms as CH_3SCH_3 , carbon disulfide, and hydrogen sulfide. Once emitted into the atmosphere these chemicals are known to be initially oxidized by already existing OH radicals. The exact role that these species play in the overall sulfur cycle is uncertain due to questions over numbers and production rates(1). The most

important source of sulfur dioxide is known to be by direct emission as a pollutant. Emissions from the combustion of sulfur containing fossil fuels are believed to be its major source given evidence indicating that the highest levels of SO_2 are found over the continental U.S. and Europe, whereas over areas of the South Pacific levels fall off greatly(1).

Although the existence of sulfur dioxide in the atmosphere can be directly adverse to one's health, the atmosphere's method of removal of these species causes the greatest harm. The sulfur is brought back to the earth as sulfate, which acidifies cloud droplets and leads to acidic rainfall. Oxidation of the sulfur dioxide to sulfur trioxide in the atmosphere is believed to occur by a number of processes(1,4). In some cases, gas-phase hydroxy radicals may oxidize the SO_2 , and the SO_3 product is then incorporated into cloud droplets and brought to the earth in the rain. Oxidation of the S(IV) species in reactions on solid aerosol surfaces has also been considered as a possible means of conversion to S(VI)(1,4). In clouds, fog, and rain, oxidation is a solution reaction occurring by the many oxidizing agents known to exist in the atmosphere. According to Moller(4), this process seems to be the major source of atmospheric SO_3 . He uses a kinetic model based on theoretical and experimental results from the literature in making this assumption. Initially the sulfur dioxide dissolves in the droplet where it is then oxidized. Since the sulfate species is more acidic than the sulfite species,

the oxidation step directly leads to the generation of a proton, thereby increasing the acidity of the cloud droplets. The cycle is completed when it rains.

Of the many means of oxidation in the liquid phase it has been theoretically proposed by Moller(4) that the conversion rate is dominated by ozone and hydrogen peroxide at the pH range of interest. Also Kok(5) has determined that the concentrations of H_2O_2 in rainwater are in fact of sufficient magnitude to contribute substantially to this oxidation process.

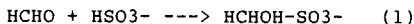
The kinetics of the oxidation of sulfur dioxide by H_2O_2 have been studied extensively at numerous temperatures and pH's in bulk solutions. Mader(6) studied the rate of oxidation at alkaline pH's and determined the reaction to be first order in peroxide and sulfite. Penkett et.al(7) in 1979 studied the same reaction at pH's of atmospheric importance, 4.0 to 6.5, and also found the rate to be first-order in peroxide and sulfite. Also, Penkett showed the rate constant to be inversely proportional to the square root of hydrogen ion concentration for ozone oxidation while the rate constant of the peroxide oxidation is directly proportional to hydrogen ion concentration. Therefore, at the lower pH's of the cloud droplets, oxidation by hydrogen peroxide dominates. Both workers found the reaction to be buffer catalyzed and subject to general acid catalysis.

Martin and Damschen(8) showed results at pH 0-2.8 and incorporated the effect of acid catalysis into a general rate

equation for application to the atmosphere. To confirm the result that hydrogen peroxide is the most important species for sulfite oxidation in the atmosphere, Kunen et.al(9) ran oxidation reactions with sulphite and H₂O₂ concentrations that were more typical of environmental levels. At these low concentrations, they found a rate constant comparable to Penkett, and Martin and Damschen.

Although considerable work has been done on the oxidation process itself, little work has been found describing inhibition of the process. Richards et.al(10) report that such an inhibition must exist. In their article reporting levels of hydrogen peroxide and sulfite in Los Angeles cloudwater, they feel an inhibition of the oxidation process must occur in order that their reported levels of sulfite be accurate. Results of Kok et.al(11) indicating that sulfite and H₂O₂ can coexist in the presence of formaldehyde even at low concentrations have confirmed Richards's belief in a possible inhibition caused by formaldehyde.

Adducts of carbonyl compounds and sulfite are known to exist in solution and are therefore presumed to exist in atmospheric cloud water in light of this evidence. An example of an adduct is the formaldehyde bisulfite addition compound.



In the measurement of HCHO in the ambient aerosol, Klippel and Warneck(12) and Dasgupta(13) have attributed higher than expected concentrations of formaldehyde to the formation of hydroxymethanesulfonic acid (HMSA), the addition product of formaldehyde and sulfite. In his measurements of particulate phase aldehydes, Grosjean(14) found much higher than predicted levels of all the carbonyls measured based on simple equilibria between aerosol droplet and gas phases. He suggests that the formation of adducts could result in the deviation.

In light of this evidence, it seems obvious that the formation of addition products of sulfite and carbonyl compounds occurs in the atmosphere and inhibits the oxidation of sulfite by hydrogen peroxide. Kok et.al(15) has shown kinetically that HMSA is in fact resistant to oxidation by H_2O_2 .

Work up to this point has centered around the formaldehyde addition product as the primary form of inhibition. However, there is evidence to suggest that addition products with higher aldehydes must also be considered if an accurate picture of the inhibition process is to be made. Recently the quantification and characterization of aldehydes and ketones has been made possible through their capture as their DNPH derivatives. Kuwata et.al(16), Kuntz et.al(17), Grosjean(14), and Schulam(18) have been able to efficiently determine levels of these compounds in ambient air. The results of Grosjean, who

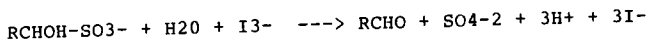
sampled the Los Angeles air, indicate formaldehyde to be the dominant carbonyl compound accounting for about 40 percent of the total carbonyl content. The remaining 60 percent is about 30 percent acetaldehyde, 12 percent propionaldehyde, 12 percent 2-butanone, 5 percent butanal, and a trace of other aldehydes. Schulam, sampling in Schenectady, found mostly formaldehyde with only about 5 percent acetaldehyde.

Recently the quantification of these compounds has been achieved in cloudwater samples. Grosjean(19) found formaldehyde to represent about 50 percent of the total carbonyl concentration with levels of acetone and acetaldehyde also significant. Bertman(20) in his work on Whiteface Mountain in New York has also found significant levels of formaldehyde, acetaldehyde and acetone in cloudwater samples.

From the data it is evident that although formaldehyde is the major representative of carbonyl compounds in the atmosphere, other aldehydes and ketones do exist which could form adducts with bisulfite, thereby, inhibiting its oxidation by hydrogen peroxide. Munger et.al(21) cites data which shows sulfite concentrations in excess of those of formaldehyde, indicating that higher aldehydes must also form adducts, in order to prevent the existing sulfite from being oxidized. Therefore, although it is important that the kinetics and equilibria of the HMSA system be studied, the role that the higher carbonyl-bisulfite adducts play in the sulfur cycle must be also considered.

The first step in understanding the chemistry of the aldehyde-bisulfite adduct formation and decomposition is the determination of an equilibrium constant for the adducts (equation 1). Data on these values is available for the formaldehyde adduct(22,15) and for the benzaldehyde adduct(23), but is unavailable for other carbonyl compounds.

In their determination of the equilibrium constant for the benzaldehyde-bisulfite adduct, Stewart and Donnolly used an iodometric titration method. Because the dissociation reaction is slow at pH 2 for these species, the determinations were made by rapidly acidifying a buffered solution and simultaneously adding an iodine solution in slight excess of the ionic sulfite.

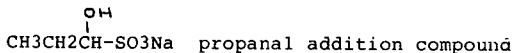
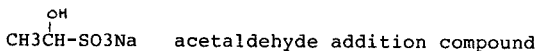


Back titration of the excess iodine with thiosulfate revealed the quantity of sulfite previously existing in solution. Determinations were made at several pH's and for various temperatures. For the pH's of atmospheric interest, they found the K_{eq} at pH 4.77 to be 1.06×10^{-4} and at pH 5.21 to be 1.00×10^{-4} .

Dasgupta measured the absorbance of free bisulfite in solution at equilibrium using ultraviolet spectrophotometry. Since formaldehyde and HMSA do not absorb significantly in the UV region, all absorption is assumed to be by the

bisulfite species. Concentrations were then calculated for bisulfite based on UV absorbance of standard bisulfite solutions. He obtained K_{eq} of 1.56×10^{-5} and 1.17×10^{-5} at pH values of 4.0 and 5.0 respectively. Kok reports data for the HMSA as well, based on kinetic data. He calculated rates of formation and decomposition by mixing solutions of HCHO and bisulfite together and taking an aliquot of this solution at selected time intervals. He then oxidized any bisulfite that was not combined as HMSA. A similar experiment determined the rate of decomposition. He calculated an equilibrium constant by dividing the rate of decomposition by the rate of formation. The values obtained are 1.0×10^{-7} and 1.5×10^{-7} at pH 4.0 and 5.0 respectively, values which differ significantly from those of Dasgupta.

This paper will report on the determination of the equilibrium constant for the acetaldehyde-bisulfite adduct. The methods of synthesis, characterization and determination of purity of the acetaldehyde adduct along with those of acetone and propanal will also be discussed.



The method used in this work is that used by Dasgupta(22). In the determination of a standard sodium sulfite calibration curve, a number of problems arose. A discussion of the cause of these problems will be given based on the physical nature of the system as described by Cotton and Wilkinson(24).

EXPERIMENTAL

CHEMICALS:

The sodium bisulfite used in the synthesis of all the addition compounds and for the standard calibration curve was obtained from the Aldrich Chemical Company.

Formaldehyde sodium bisulfite addition compound was obtained from the Aldrich Chemical Company for purposes of comparing purity of samples produced in the lab.

When producing the formaldehyde sodium bisulfite addition compound in the lab, paraformaldehyde purchased from the Baker Chemical Company was used. Freshly distilled acetaldehyde was used in producing the acetaldehyde addition compound. For the acetone addition compound and the propionaldehyde addition compound, initial purification of the carbonyl compound was not attempted.

INSTRUMENTATION:

Bisulfite and Acetaldehyde Absorbances: The absorbances used in making the standard calibration curves and in determining the equilibrium constant were taken using a Perkin-Elmer Lambda 3B UV/VIS spectrophotometer interfaced with a

Perkin-Elmer 3600 microcomputer. A 10 cm quartz window absorption cell was utilized in all runs. The compartment of the spectrophotometer was modified to accommodate these cells since the instrument was only made for 1 cm cells.

NMR Spectra: All spectra were taken on a Hitachi-Perkin Elmer high resolution NMR spectrometer, model R-24A. This is a 60 MHz instrument. In all cases, D₂O was used as the solvent.

BISULFITE ADDITION COMPOUNDS:

Preparation: Approximately 350 ml of a saturated solution of sodium bisulfite, corresponding to about 0.4 moles of aldehyde, was prepared in a 50:50 ethanol to water solution. This solution was then cooled to 0 C in an ice bath and any excess bisulfite was filtered off. Approximately 0.6 moles of the desired aldehyde or ketone was cooled and added slowly with constant stirring to the saturated solution. Precipitation of the addition compound was achieved through the addition of a large excess, usually about 500 ml, of ethanol. The precipitate was recovered using suction filtration through a Buchner funnel. In many cases, the filtrate still contained large amounts of the addition compound due to physical limitations on the amounts of ethanol used when precipitating. Therefore readdition of ethanol to the cooled filtrate often produced more product.

Attempts at recrystallization were made in methanol, ethanol, tetrahydrofuran, and ethyl acetoacetate, but due to

the high ionic character of the adducts, no success was achieved. The melting point of the acetaldehyde addition compound was found to be in excess of 340 C.

Characterization and Purity Determination: Verification that the desired addition compound did form was done using NMR. Because purification of the samples could not be achieved by recrystallization, attempts were made to directly determine the purity of the addition compounds synthesized. A determination of the total bisulfite concentration was attempted by dissolving the compounds in 2 M NaOH, since it is known that the adducts easily decompose in alkaline solution(23). The bisulfite concentration was measured using UV spectrophotometric absorption at 256 nm.

A purity determination using NMR integrations was also attempted. Better success was achieved using this method and all percent impurities were determined in this fashion. Results and a discussion of the method are given in the Results and Discussion section.

CALIBRATION CURVES:

To control the pH of all solutions, an acetic acid/sodium acetate buffer was utilized. Since the pKa of acetic acid is 4.76 and the pH desired was 4.7, an equimolar solution of the two species was prepared. This buffer also served to control the ionic strength at approximately 0.12. Verification of the pH was done with a pH meter.

In the determination of the equilibrium constant for the formaldehyde bisulfite addition product, Dasgupta(22) assumed all ultraviolet absorption was due to bisulfite since the HMSA and formaldehyde do not significantly absorb in this region. Since acetaldehyde does absorb in the same area as the bisulfite it was necessary to construct a calibration curve for acetaldehyde at the wavelength of interest, namely 256 nm. Solutions of acetaldehyde were made ranging in concentration from 1×10^{-1} M to 2.75×10^{-3} M at pH 4.7 and an absorption coefficient was found using Beer's Law (Figure 1).

A calibration curve was also constructed for sodium bisulfite in order to determine its absorption coefficient at 256 nm and pH 4.7. The concentrations utilized in this case ranged from 1.0×10^{-1} M to 6.73×10^{-4} M. Initially, random readings were found at the lower concentrations and an interference due to oxidation of the bisulfite was assumed (see Figure 2). Addition of approximately 50 mg of catalase to 2 L of the buffer solution alleviated this problem. In constructing this curve, problems were also encountered at the high concentrations (Figure 2). As mentioned in the introduction this problem has been attributed to the physical nature of the bisulfite ions. Further explanation will be given in the discussion. An absorption coefficient was determined using Beer's Law plot in a concentration range from 1.2×10^{-2} M to 1.35×10^{-3} M (Figure 3).

DETERMINATION OF EQUILIBRIUM CONSTANT:

As stated in the introduction, the method adopted was that used by Dasgupta in his determination of an equilibrium constant for the formaldehyde bisulfite addition compound(22). For this equilibrium constant determination of the acetaldehyde addition compound, a pH of 4.7 was used with acetate as the buffer. Solutions of the addition compound were made at concentrations of 5×10^{-1} M to 3.1×10^{-2} M in the acetate buffer. All solutions were filtered through millipore filters to remove any fine particles. Because dissociation was usually around 1%, 10 cm cells were used in order to obtain absorptions in a workable range. Absorption coefficients for the acetaldehyde and sodium bisulfite were found using calibration curves of standard solutions, as stated. The water used for the solutions was deionized and purged with nitrogen. Also, to remove any problems resulting from the oxidation of the free bisulfite by hydrogen peroxide in the buffer, approximately 50 mg of catalase was added to 2 L of the buffer. The actual equilibrium constant was found by graphing the concentration of the complex versus the square of the concentration of acetaldehyde at equilibrium. The slope of this line gave the equilibrium constant (Figure 4).

RESULTS AND DISCUSSION

Characterization of the Bisulfite Addition Compounds: Verification that the desired addition compound did form was done using NMR. In formation of an adduct the bisulfite ion attacks the aldehyde or ketone at the carbonyl carbon and the carbonyl functional group is converted to a hydroxyl group. In all cases, therefore, the absence of any aldehydic protons is important in verifying that adduct formation does in fact occur. Also, verification that the salt precipitated with the addition of ethanol is not free bisulfite, is found in examining the peaks not attributable to the acidic proton of bisulfite.

For the formaldehyde addition compound the NMR shows that an adduct did indeed form since there is no evidence of an aldehydic proton (Appendix A). Assignment of peaks in the spectrum is difficult, however, due to a large water impurity. The peaks present at 4.6 ppm and at 4.7 ppm (see Table 1) qualitatively fit the structure of this addition compound which does contain two distinct types of hydrogens. One peak occurs as the result of absorption by the hydroxyl proton and the other occurs as the result of absorption by the two protons on the old carbonyl carbon. Integration is meaningless presumably due to a water contamination.

An NMR spectrum was also taken on the formaldehyde bisulfite addition compound purchased from Aldrich in order to compare with that produced in the laboratory(Appendix B). The peaks which occur agree qualitatively with those of the laboratory sample (Table 1). Integrations were taken of this spectrum and allowed assignment of specific peaks. Because the integration of the peak at 4.6 ppm is almost half that at 4.5, if an H₂O contamination of the D₂O is taken into account, the peak at 4.6 is assumed to result from the hydroxyl proton.

For the acetaldehyde addition compound, NMR again proves to be a valuable aid in characterization(Appendix C). The spectrum shows two distinct areas of absorption (Table 1). Although the peak at 4.9 ppm is described as a quartet, it must be added that a strong singlet overlays it. The absence of any aldehydic proton indicates that an addition compound did form. For free acetaldehyde, the doublet that occurs due to the methyl hydrogens is at 2.2 ppm. For the adduct, this absorption seems to have shifted to 1.8 ppm. The shift seems reasonable if it is realized that formation of an adduct should decrease the polarity of the adjacent carbon from a carbonyl carbon to a hydroxyl bonded carbon, thereby, allowing more shielding to occur for these hydrogens.

Given the structure of this adduct as given in the introduction this splitting pattern seems reasonable as well. The proton which was the aldehydic proton in acetaldehyde causes the doublet splitting. Likewise, this proton is split

by the methyl hydrogens into a quartet. Decoupling experiments on these hydrogens verified this assumed splitting pattern. The singlet overlaying this quartet is assumed to be the hydroxyl proton.

For the acetone addition compound, NMR again verified adduct formation(Appendix D). Pure acetone shows a single peak at 2.2 ppm, while the spectrum of the adduct shows a shift upfield to 1.6 ppm (Table 1). Once again this shift can be explained in terms of the decrease in polarity of the adjacent carbon. Also, a peak was seen at 4.8 ppm indicating the presence of a hydroxyl proton.

For the NMR spectrum of the propionaldehyde addition compound, similar results are found(Appendix E). The adduct spectrum shows no aldehydic proton as seen in pure propionaldehyde and a hydroxyl proton is present in its place. Also, the quartet and triplet which exist at 2.4 ppm and 1.2 ppm respectively in the spectrum of pure sample are shifted upfield in the adduct spectrum.

Purity Determination of the Addition Products: As mentioned earlier, because purification of the samples could not be achieved by recrystallization, it was necessary to determine the purity of the adducts if an accurate determination of equilibrium constants was to be made. It was assumed that there was no free bisulfite as a contaminant because in the preparation, an excess of aldehyde was always used often double what was actually required. Also, because all the

aldehydes used were liquids and any product isolated was solid, the adducts were assumed to be free of aldehyde contamination. This was shown to be true since no aldehydic absorption was seen in the NMR spectra.

Originally, it was hoped that a measure of the total bisulfite concentration could be made by breaking the adducts apart in strong base and measuring the resulting UV absorption. This concentration of bisulfite could then be compared to the concentration of bisulfite which should exist if the addition compound was assumed to be free of contamination. A difference in the two concentrations would reveal the amount of impurity. Problems resulted with the aldehydes existing in basic solution where aldol condensations occurred. The products of the condensation reactions are highly conjugated systems and therefore hid the absorption of the bisulfite ion. Because the aldol condensation occurs quite fast, as witnessed by an almost immediate presence of yellow in the solution upon addition of the base, attempts at making measurements immediately after mixing also proved unsuccessful.

As mentioned earlier, integrations from the NMR spectra appeared illogical. Comparison of the four spectra, however, shows that an excess of hydroxyl type protons appears universal. This finding seemed to indicate a contamination due to hydration of the adducts. In fact the label of the formaldehyde addition compound purchased from Aldrich indicates the compound to be hygroscopic. Also, the

integrations of this compound seem reasonable if the H₂O contamination in the D₂O is subtracted from the integration of the hydroxyl proton. Therefore it seems apparent that a water contamination does exist and, as would be expected for -OH absorptions, appears in all spectra to coincide with the absorption of the hydroxyl proton.

The actual percent impurity was determined using a comparison of the integration values of the various peaks from the NMR spectrum. Based upon the absorption of a single hydrogen which is found in the integration of the alkyl part of the adduct spectrum, it is fairly easy to determine the number of excess hydrogens existing in the sample. Conversion of excess hydrogens to moles of water gave the percent impurity.

Example using a spectrum of the acetaldehyde adduct: The doublet at 1.8 ppm represents 3 H's and has an integration of 2.4 cm. The quartet at 4.9 ppm represents 2 H's plus any H's due to an impurity and integrates at 4.9 cm. The impurity due to water in the D₂O is 0.5 cm, therefore 4.4 cm is actually due to the quartet. From the doublet data one H should be 0.8 cm. Based on the structure of the adduct, the quartet overlaid by the singlet should in fact be two H's with an integration of 1.6 cm. The integration therefore shows an excess of 2.8 cm, presumably due to water. This integration corresponds to 3.5 H's or 1.75 moles of H₂O, which is a 20% impurity.

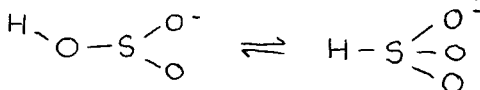
The actual amount of impurity varied from sample to

sample and could be controlled by drying the sample or by making sure the aldehyde and the saturated bisulfite solution were cooled before mixing. Impurities of as low as 5% were eventually achieved for the acetaldehyde adduct. Impurities of the acetone adduct were as low as 2%, while in the only batch of propanal adduct prepared an impurity of 18% was found.

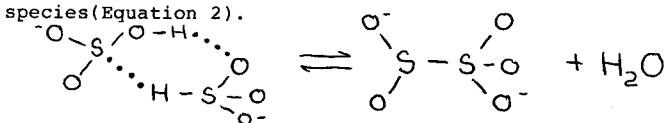
The Calibration Curve for Sodium Bisulfite: When absorption measurements were first taken from standard solutions of sodium bisulfite, there was a considerable lack of linearity at the low concentrations and at the extreme high concentrations (Figure 2). The deviations at the low concentrations were eventually assumed to result from oxidation of the bisulfite by oxidants, either O_2 or H_2O_2 , present as impurities in the buffer solution. As a result nitrogen was bubbled through a 2 L sample of the buffer to remove any dissolved oxygen. Since oxidation by hydrogen peroxide occurs much more quickly than O_2 oxidation, even a small amount of H_2O_2 could cause problems. As stated in the experimental section this problem was alleviated by addition of 50 mg of catalase to the 2 L of buffer. These precautions stabilized absorptions in the lower range of concentrations used (Figure 3).

The problems at the higher range of concentrations could not be eliminated but are explained by the activity of the bisulfite ions in solution(24). At low concentrations, 3 x

10⁻³ M, tautomers exist of the bisulfite ion (Equation 1).



However, at higher concentrations, 1 x 10⁻² M, hydrogen bonding begins to occur. Also in this range, the hydrogen bonded species exist in equilibrium with an S-S bonded species (Equation 2).



For the absorptions measured, linearity was achieved up to about 2.3 x 10⁻² M whereupon absorptions seemed to become greater than expected (Figure 2). In light of the evidence concerning the change in species at higher concentrations as well as the fact that at higher concentrations Beer's Law is no longer obeyed, the nonlinearity at the higher concentrations seems reasonable. It must be added that because dissociation of the adducts is small, the concentrations of bisulfite existing in solution never reached the range of nonlinearity.

Determination of the Equilibrium Constant for the Acetaldehyde Bisulfite Addition Compound: The first method attempted for determining the equilibrium constant of the acetaldehyde addition compound was unsuccessful. Initially, solutions of varying concentrations of acetaldehyde and bisulfite were made in an acetate buffer at pH 4.7. It was hoped that as the concentrations of acetaldehyde increased,

formation of the addition compound would lead to a progressive decrease in UV absorption. The equilibrium constant could then be determined once these absorptions were converted to concentrations. The reasons this method did not prove successful are unknown but could be attributed to an improper choice of concentration range.

A successful determination was achieved as stated by employing the method of Dasgupta(22) with modifications where necessary. Since both sodium bisulfite and acetaldehyde absorb in the UV region of interest, namely 256 nm, the absorbance measurements taken were assumed to be the combination of both species. It was also assumed that the addition compound did not absorb because it has no nonbonding electrons on sulfur. As mentioned in the experimental section it was necessary to use 10 cm cells in taking absorptions because dissociation of the addition compound was quite small. Dasgupta used concentrations of adduct ranging from 1×10^{-1} to 1×10^{-3} M. In this work starting concentrations were approximately five times this value in order to obtain any substantial absorptions. When the concentrations of Dasgupta were used absorptions were too low to be measured even when the 10 cm cells were employed. Since in this work, both the acetaldehyde and bisulfite contributed to the total absorption, it is unknown why Dasgupta was able to measure significant absorptions at his concentrations even though bisulfite was the only absorbing species for the formaldehyde adduct. Absorption coefficients

for the acetaldehyde and sodium bisulfite were found using calibration curves of standard solutions at pH 4.7 (Table 2). The equilibrium constant obtained from the slope of the Figure 4 is 6.3×10^{-5} . The correlation coefficient for this line is .9993 indicating a high degree of linearity.

Comparison of Equilibrium Constants: Considering the equilibrium constants obtained for the formaldehyde addition compound and the benzaldehyde addition compound by Dasgupta and Stewart and Donnally, respectively, (Table 3), the value obtained in this work seems reasonable. From these three constants it also appears that the equilibrium follows a trend based upon structure. Although the pH's used in the three cases are slightly different, the values do not seem to change much within the range presented here. It appears that as the size of the aldehyde increases, the equilibrium constant also gets larger. A similar trend, from formaldehyde to acetaldehyde to benzaldehyde was shown in the rates of decomposition of these adducts in work done by Blackadder and Hinshelwood(25). The decomposition rates they report are 5.5×10^{-6} for formaldehyde, 2.5×10^{-4} for acetaldehyde, and 7.7×10^{-3} for benzaldehyde. Therefore the fact that the equilibrium constants should follow a similar trend is reasonable.

The value reported by Kok et.al for HMSA, seems out of place from the three other values listed. Kok et.al(15) feel their value is more accurate because it is based upon larger

changes in chemical composition. As the numbers relate to the stability of the aldehyde bisulfite compounds existing in clouds and rainwater, however, it is obvious that both the formaldehyde adduct and the acetaldehyde adduct will not decompose purely by hydrolysis once they are present in cloudwater.

In order to successfully model the role of these aldehydes on the oxidation of S(IV), rates of decomposition and formation of the acetaldehyde adduct must be found. Equilibrium constants, and rates of decomposition and formation must also be investigated for acetone, propanal, 2-butanone and benzaldehyde, the other major carbonyl compounds found in the atmosphere. In addition, some interesting kinetic work could be done by investigating the oxidation of S(IV) by hydrogen peroxide in solution in the presence of these carbonyl compounds.

Table 1: Characteristics of the NMR Spectra For the Bisulfite Addition Compounds Examined

<u>Compound</u>	<u>Peak(ppm)</u>	<u>Integr.(cm)</u>
formaldehyde(Aldrich)	s 4.5	6.8
	s 4.6	4.5
formaldehyde(lab.)	s 4.6	---
	s 4.7	---
acetaldehyde	d 1.8	2.4
	q 4.9	4.9
acetone	s 1.6	4.3
	s 4.8	1.0
propanal	t 1.1	4.9
	m 1.9	3.2
	m 4.2	2.9
	s 4.8	4.9

s=singlet d=doublet t=triplet q=quartet m=multiplet

Table 2: Absorption Coefficients from Calibration Curves

<u>Compound</u>	<u>Wavelength (nm)</u>	<u>Absorption</u> <u>Coeff. (molarity/cm)</u>
Sodium Bisulfite	256.0	2.17
Acetaldehyde	256.0	4.64

Table 3: Equilibrium Constants for Some Aldehyde Bisulfite Addition Compounds

<u>Worker</u>	<u>Compound</u>	<u>Method</u>	<u>pH</u>	<u>constant (mol/L)</u>
Stewart and Donnally	benzaldehyde	iodometric titration	4.77	1.06×10^{-4}
Stewart and Donnally	benzaldehyde	iodometric titration	5.21	1.00×10^{-4}
Dasgupta et.al	formaldehyde	UV absorption	4.0	1.56×10^{-5}
Dasgupta et.al	formaldehyde	UV absorption	5.0	1.17×10^{-5}
Kok et.al	formaldehyde	kinetic calculation	4.0	1.0×10^{-7}
Kok et.al	formaldehyde	kinetic calculation	5.0	1.5×10^{-7}
This work	acetaldehyde	UV absorption	4.7	6.3×10^{-5}

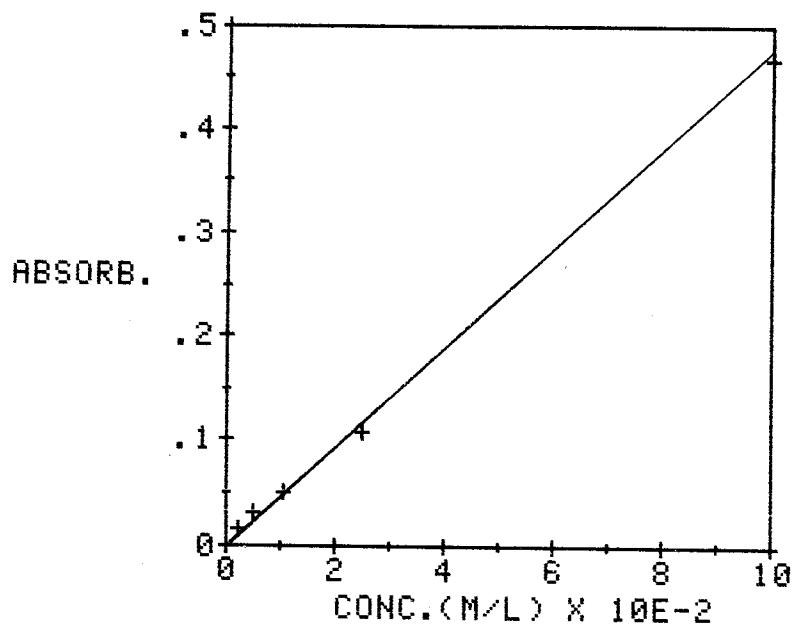


Figure 1: Calibration curve for acetaldehyde at pH 4.7 and 256 nm

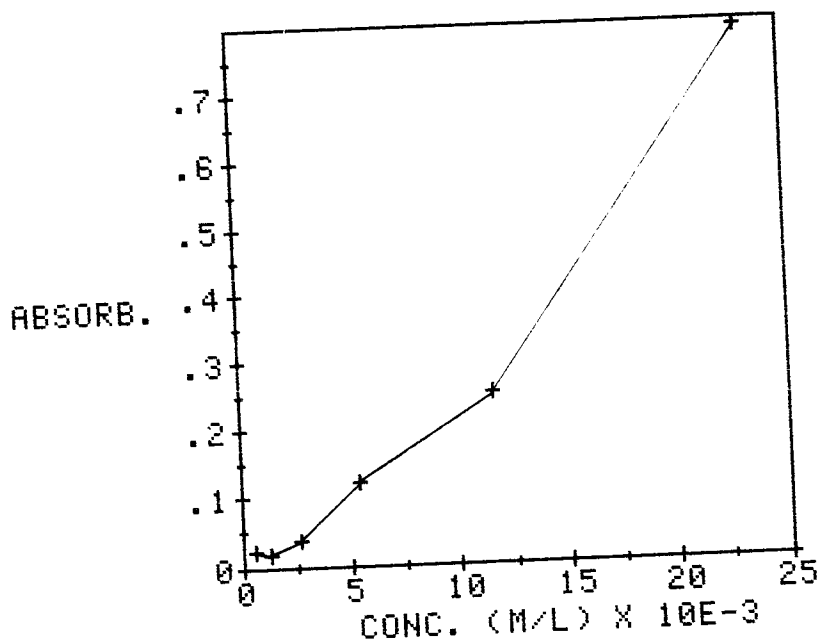


Figure 2: First calibration curve for sodium bisulfite at pH 4.7 and 256 nm.

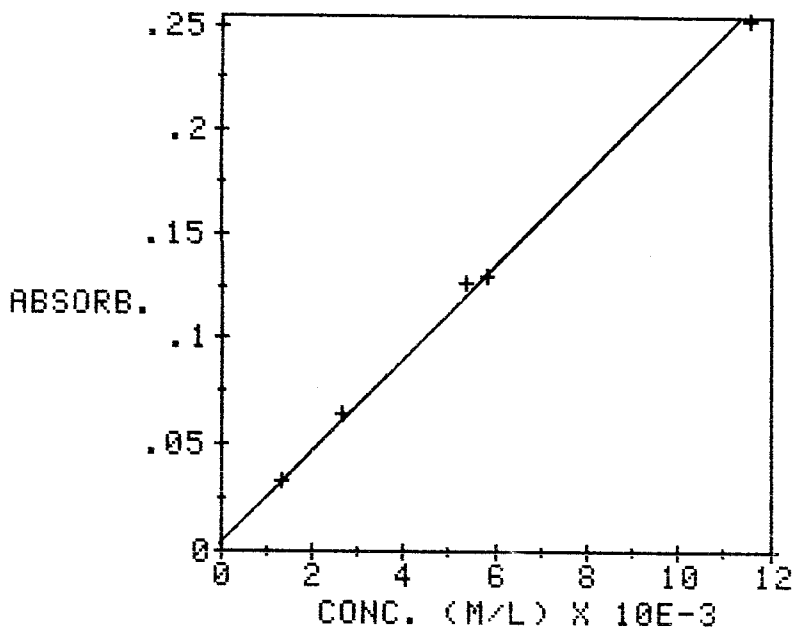


Figure 3: Second calibration curve for sodium bisulfite at pH 4.7 and 256 nm.

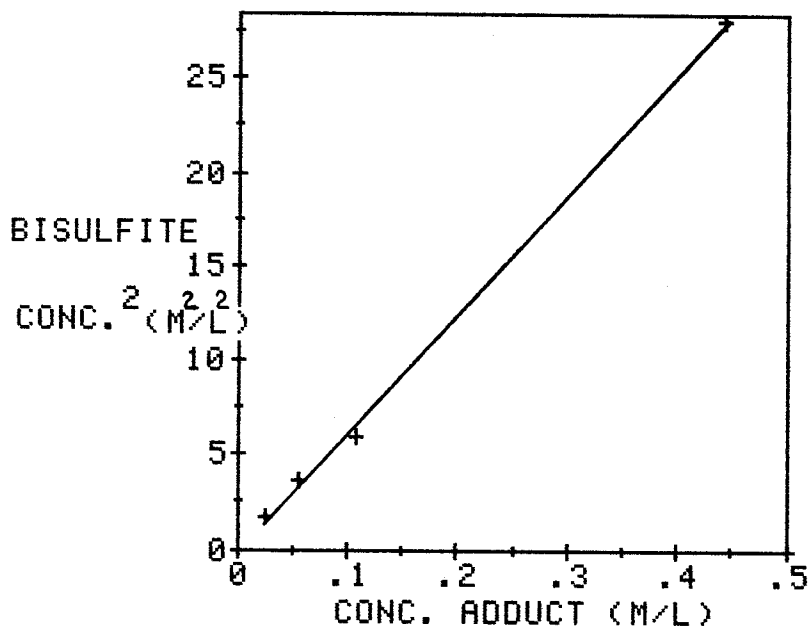


Figure 4: Bisulfite concentration² vs. adduct concentration

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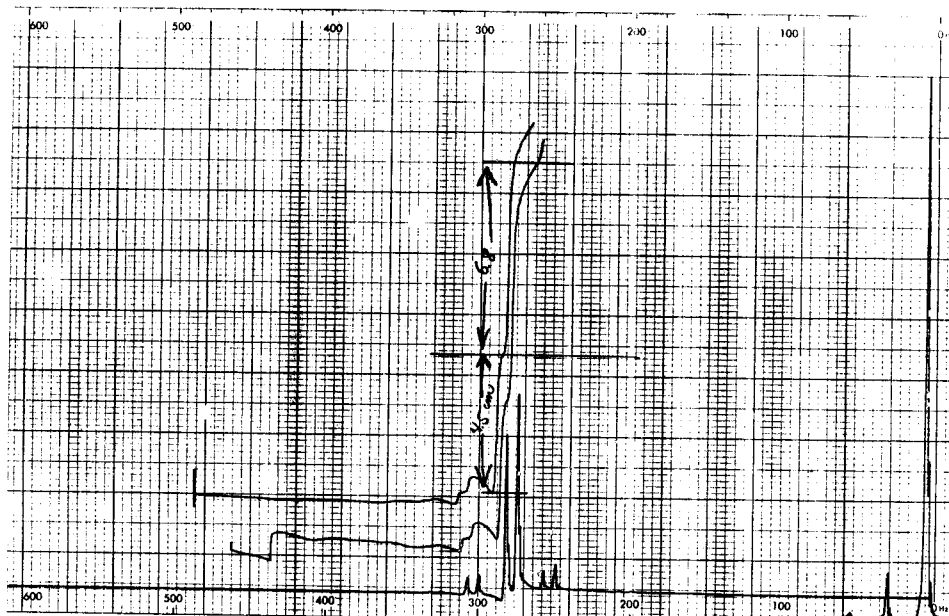
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1H SPECTRUM NO.

SAMPLE Aldrich 6m-30,
1/21/85

Appendix B

REFERENCE: TMS
SOLVENT: D₂O
CONC: 1M
AMPLITUDE:
SPECTRUM: 4
INTEGRAL: 9

H1 LEVEL:

H1 NORM LO HI

H2 LEVEL:

GAIN:

X1 X10

SWEEP WIDTH:

600 300 150 75 37.5 18.75 9.375 4.6875

FILTER M1

CRC NOR

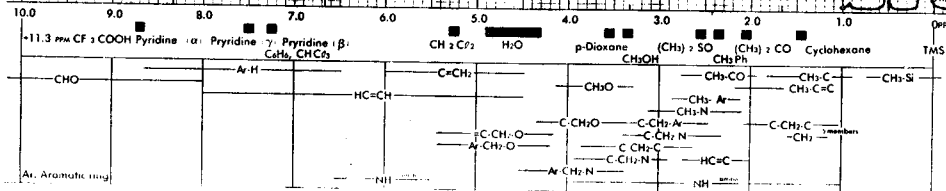
SWEEP TIME

☒ 300/150 SEC ☐ SEC

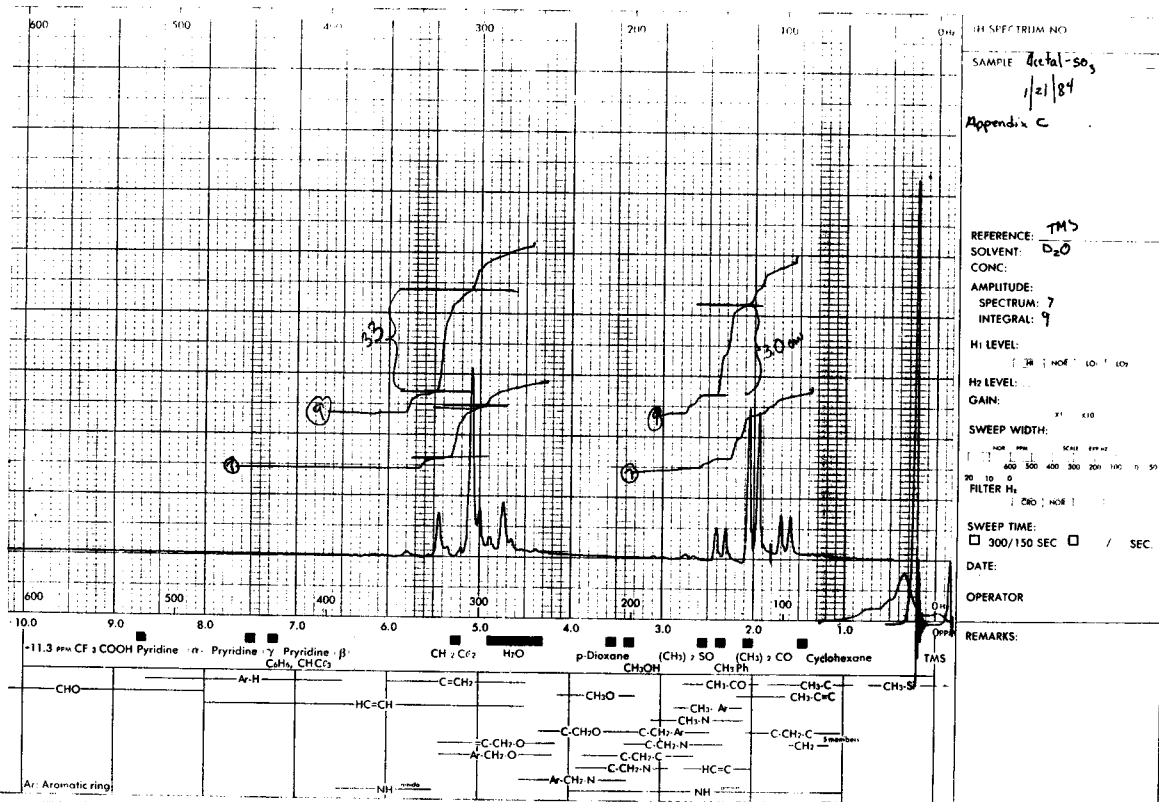
DATE:

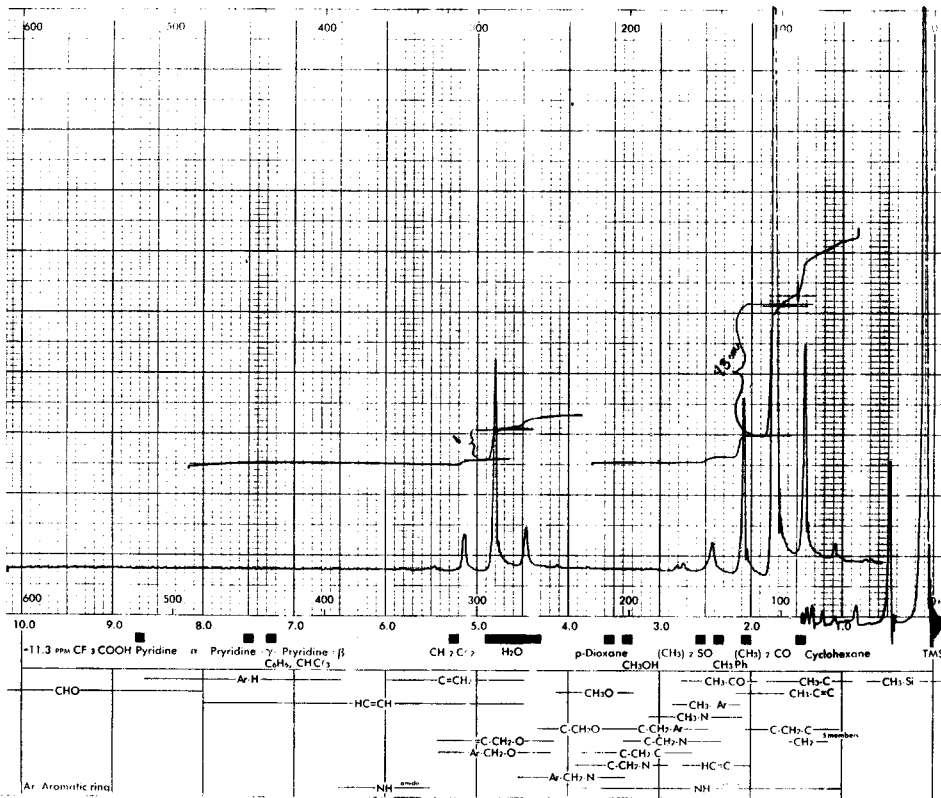
OPERATOR

REMARKS:



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1H SPECTRUM NO.:

SAMPLE: A. etnu-30g

Appendix D

REFERENCE: TMS

SOLVENT: D₂O

CONC:

AMPLITUDE: 7

SPECTRUM: 7

INTEGRAL: 7

H₁ LEVEL:

H₂ LEVEL:

GAIN:

SWEEP WIDTH:

FILTER M₁:

SWEEP TIME

☐ 300/150 SEC ☐ / SEC.

DATE:

OPERATOR

REMARKS:

